Impacts of Biomass Burning in Southeast Asia on Ozone and Reactive Nitrogen over the Western Pacific in Spring

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Abstract

Aircraft measurements of ozone (O_3) and its precursors (reactive nitrogen, CO, non-methane hydrocarbons) were made over the western Pacific during the Transport and Chemical Evolution over the Pacific (TRACE-P) campaign, which was conducted during February-April 2001. Biomass burning activity was high over Southeast Asia (SEA) during this period (dry season) and convective activity over SEA frequently transported air from the boundary layer to the free troposphere, followed by eastward transport to the sampling region over the western Pacific south of 30°N. This data set allows for systematic investigations of the chemical processes in the outflow from SEA. Methyl chloride (CH_3Cl) and CO, which were well correlated with hydrogen cyanide (HCN) and methyl cyanide (CH_3CN), are chosen as a primary and secondary tracers, respectively, to gauge the degree of the impact of emissions of trace species from biomass burning. Biomass burning is found to be a major source of reactive nitrogen and O_3 in this region from correlations of these species with the tracers. Changes in the abundance of the major components of reactive nitrogen (NO_x, PAN, HNO_3, and nitrate) during upward transport are quantified from the altitude change of the slopes of the correlations of these species with CO. NO_x decreased with altitude due to its oxidation to HNO_3. On the other hand, PAN was conserved during transport from the lower to the middle troposphere, consistent with its low water solubility and chemical stability at low temperatures. Large losses of HNO_3 and nitrate, which are highly water soluble, occurred in the free troposphere, most likely due to wet removal by precipitation. Increases in the mixing ratios of O_3 and its precursors due to the biomass burning in SEA are estimated using the tracers. Enhancements of CO and total reactive nitrogen (NO_y), which are directly emitted from biomass burning, were largest at 2-4

km. At this altitude, the increases in NO_y and O_3 were 580 parts per trillion by volume (pptv) (150%) and 19 parts per billion by volume (ppbv) (50%), respectively. The slope of the O_3-CO correlation and O_3 production efficiency in biomass burning plumes were similar to those observed in fire plumes in northern Australia and Africa/South America. This similarity is useful in understanding the overall net O_3 production by biomass burning. Comparison of the net O_3 flux across the western Pacific region and total O_3 production due to biomass burning in SEA suggests that a majority of O_3 produced was transported to the western Pacific.

1. Introduction

Biomass burning is an important source of many trace gases (e.g., nitrogen oxides (NO_x), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), non-methane hydrocarbons (NMHCs), oxygenated organic compounds, sulfur dioxide (SO_2), and methyl chloride (CH_3Cl)) [*Crutzen and Andrea*, 1990; *Andrea et al.*, 1996; *Blake et al.*, 1996; *Andreae and Marlet*, 2001; *Yokelson et al.*, 2003]. Reactions of these trace gases lead to the formation of O_3 and aerosols, which strongly influence chemical environments and radiation budgets on regional and global scales. Generally, biomass burning occurs most extensively in tropical and subtropical regions. Emissions of NO_x and CO from Africa and South America constitute a large fraction of global biomass burning emissions, and those from Southeast Asia (SEA), Indonesia, and Australia also make substantial contributions [*Galanter et al.*, 2000].

The impacts of biomass burning on tropospheric chemistry over Africa, South America, Indonesia, and Australia have been widely studied by ground-based and airborne measurements [e.g. *Fishman et al.*, 1996; *Harriss et al.*, 1988; 1990; *Lindesay et al.,* 1996; *Blake et al.*, 1999; *Thompson et al.*, 2001; *Kondo et al.*, 2002; *Takegawa et al.*, 2003a; 2003b]. By contrast, studies of the effects of biomass burning in SEA on regional chemical composition are very limited. *Elvidge and Baugh* [1996] identified peninsular SEA (primarily Thailand, Myanmar, Laos, Cambodia, and Vietnam) and east-central India (Orissa Province) as the two major areas of biomass burning in SEA and India in February-March using satellite remote sensing data. Increases in O_3 in plumes impacted by biomass burning over SEA in spring were detected by ozonesonde measurements over Hong Kong and aircraft sampling during the Pacific Exploratory Mission (PEM)-West-B [*Chan et al.*, 2000; 2002]. Ground-based measurements of CO

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and O_3 in Thailand indicated effects of biomass burning on these species in the dry season [*Pochanart et al.*, 2001; 2003]. The spatial extent of the effects of biomass burning strongly depends on transport processes, especially transport from the boundary layer to the free troposphere as well as chemical processes. Emissions of trace species from biomass burning and their chemical and transport processes need to be understood in order to assess the overall impact of biomass burning in this region on the chemical environment over the western Pacific. However, there have been no simultaneous measurements of key species to enable this investigation. In this study, we have investigated these processes and assessed the impacts of biomass burning by using chemical data obtained by aircraft measurements during the Transport and Chemical Evolution over the Pacific (TRACE-P) campaign.

2. Aircraft Data

In situ chemical data obtained on board the NASA P-3B and DC-8 aircraft were used in this study, including CO, CH_3Cl, hydrogen cyanide (HCN), methyl cyanide (CH_3CN), tetrachloro ethane (C_2Cl_4), NO_x, NO_y, PAN, HNO_3, aerosol nitrate (NO_3^-), aerosol size distribution, NMHCs, O_3, and H_2O. The techniques and accuracies of these measurements are summarized by *Miyazaki et al.* [2003], *Coleman et al.* [2001], *Singh et al.* [2003], *Talbot et al.* [2003], and *Clarke et al.* [2003]. The measurements of NO_3^-, HNO_3, and NO_y are explained here because of differences in the techniques used for the measurements on board the P-3B and DC-8.

Concentrations of NO_3^- in aerosol were measured on board the P-3B by the Particle into Liquid Sampler (PILS) [*Weber et al.*, 2001; *Orsini et al.*, 2001; *Ma et al.*, 2003a]. The particle collection efficiency of PILS was 90% for diameters smaller than 0.7 μm

and decreased to 50% at 1.2 μm. The collection efficiency for diameters larger than 3

μm was close to zero. On board the DC-8, the NO_3^- concentration was measured by

filter sampling, followed by ion chromatographic analysis [*Dibb et al.*, 2003].

   HNO_3 was measured by a chemical ionization mass spectrometer [*Mauldin et al.*,

1998] on board the P-3B and therefore it represents gas-phase HNO_3. On board the

DC-8, HNO_3 was collected by mist chamber, followed by ion chromatographic analysis

[*Dibb et al.*, 2003]. NO_3^- in fine particles with diameters smaller than about 1-2 μm is

considered to be included in these measurements due to small NO_3^- loss in the inlet

system upstream of the mist chamber.

   On board the P-3B, NO_y was measured by a chemiluminescence technique combined

with a gold catalytic converter heated at 300°C [*Kondo et al.,* 1997; 2003]. The inlet

was made of a 3/8-inch outer diameter Teflon tube directed rearward. A simple

aerodynamic calculation indicates that fine aerosols were rejected by this sampling

configuration, although the estimate of the size cutoff is crude. In addition, a more

detailed study shows that the concentrations of NO_3^- in fine aerosols measured by PILS

agreed well with the values of NO_y - (NO_x + HNO_3 + PAN) (Miyazaki et al.,

manuscript in preparation, 2003). These results are consistent considering that the

cutoff size of the nitrate aerosol sampled by the two instruments is similar and that

ammonium nitrate evaporates when heated at 300°C. Therefore, for the present

analysis, the direct NO_y measurements on board the P-3B are considered to represent

gas-phase NO_y + NO_3^- in fine aerosols. Because NO_y was not directly measured on

board the DC-8, we defined NO_y as the sum of independently measured NO_x (NO +

model calculated NO_2), PAN, and HNO_3.

3. Biomass Burning Activity in SEA

Areas of active biomass burning in SEA during TRACE-P can be identified by the hot spot data observed from the satellite sensor Along Track Scanning Radiometer (ATSR-2), as shown in Figure 1a. A hot spot is defined as a region where blackbody brightness temperature (T_{BB}) is higher than 312K at night. Biomass burning was most frequent at latitudes of 10°-30°N in SEA and India. The median numbers of hot spots observed at 10°-30°N and 70°-120°E in each month during 1996-2001 are shown in Figure1b. The data for 2001 are also shown in this figure. Biomass burning activity in this region generally exhibits an annual maximum in February-April. A more detailed comparison of biomass burning activities for 2001 versus climatological estimates was made by *Heald et al.* [2003].

We used two chemical tracers to distinguish biomass burning plumes from urban pollution plumes. CH_3Cl has been used as a tracer of the combustion of biomass and biofuel, and C_2Cl_4 as an industrial tracer [*Blake et al.*, 1996; *Blake et al.*, 1999]. Their relatively long lifetimes of 1.3 and 0.4 years, respectively [*Keene et al.*, 1999], allow them to be used to identify long-range transport. The concentrations of these species were quantified from whole air samples collected on both the P-3B and DC-8. Representative background values for CH_3Cl and C_2Cl_4 during TRACE-P were 550 pptv and 3 pptv, respectively. HCN and CH_3CN are also known to be emitted predominantly from biomass burning [*Andreae and Marlet*, 2001]. These species were measured only on the DC-8. Consistently, CH_3Cl was highly correlated with HCN and CH_3CN over the whole Pacific, especially above 2 km during TRACE-P [*Singh et al.*, 2003], confirming that CH_3Cl is a good tracer for biomass burning.

The horizontal distributions of these tracers at 2-4 km (lower troposphere; LT) over the western Pacific are shown in Figure 2. The air masses with high CH_3Cl (> 600 parts per trillion by volume, pptv) were mostly observed at 17°-30°N, while those with high C_2Cl_4 (up to 15 pptv) were observed mainly north of 30°N. The same features were observed at 4-8 km (middle troposphere; MT) and 0-2 km (boundary layer; BL), although they are not shown. These results show that air masses sampled at 17°-30°N were strongly influenced by biomass burning, while those sampled north of 30°N were influenced by industrial activities. *Ma et al.* [2003b] investigated the influence of biomass burning on fine particles for the regions investigated by the P-3B during TRACE-P. Using fine particle potassium (K^+) as a biomass or biofuel burning tracer, they found evidence for a biosmoke influence throughout the TRACE-P region investigated. They speculate that at the higher latitudes where the biosmoke tracer (K^+) is highly correlated with aerosol components associated with industrial emissions, such as sulfate, the source may be the use of biofuels. For the present study, we focus on the data obtained in the region of 17°-30°N and 110°-150°E as marked in Figure 2, which is referred to as the study region.

4. Meteorological Conditions and Air Mass Classification

The meteorological conditions during TRACE-P are described in detail by *Fuelberg et al.* [2003]. Here we highlight specific points relevant to the present analysis. The mean streamlines at 850 hPa (BL), 700 hPa (LT), and 500 hPa (MT) in March 2001 were calculated using National Centers for Environmental Prediction (NCEP) reanalysis data and are shown in Figure 3. At 700 and 500 hPa, the strong north-westerlies at latitudes higher than 30°N were associated with the polar jet. Air over

peninsular SEA entered the study region along the clockwise flow associated with the subtropical high-pressure system and westerlies dominating in the study region.

At 850 hPa, warm air from the prevailing anticyclone centered in the central Pacific (shown in Figure 1 of *Miyazaki et al.* [2003]) moved into this region from the south, as seen in Figure 3. It converged with cold air originating from the Siberian anticyclone over SEA in March, which is the monsoon transition period from the dry to wet season. The instability of air associated with this convergence led to occasional convection as seen from the precipitation map shown by *Miyazaki et al.* [2003]. The convection is also seen from the cloud height determined by the T_{BB} observed by the Geostationary Meteorological Satellite (GMS). We selected optically thick clouds by using GMS-infrared (IR) data for two different wavelengths (10.5-11.5 μm and 11.5-12.5 μm). The T_{BB} over the peninsular SEA frequently reached 270°K (4-5 km) and occasionally 210°K (13 km). The importance of convection over SEA in spring in transporting trace species emitted by biomass burning is also discussed in *Liu et al.* [2003].

The flow fields shown in Figure 3 largely determined the origins of air masses sampled in the study region. Figures 4a-4c show the 5-day back trajectories of air masses sampled in the BL, LT, and MT. These trajectories were calculated by the Florida State University (FSU) Kinematic Trajectory Model [*Fuelberg et al.*, 2003] using European Centre for Medium-Range Weather Forecasts (ECMWF) meteorological data. Sampled air masses were classified into 4 categories based on these trajectories. SEA air masses were defined as those passing over the intense biomass burning region south of 28°N. Northeast Asian (NEA) air masses are those transported from north of 28°N over the Asian continent to the study region at 17°N-

30°N. Air masses passing over the two regions (north and south of 28°N) on the Asian continent were classified as a mixture of SEA and NEA air masses. This air was excluded from the present analysis. Maritime air masses were transported from over the Pacific without passing over the Asian continent. They had remained in the study region for five days prior to being sampled. The probability of sampling of different types of air masses changed with altitude. SEA air masses were dominant in the LT and MT, while NEA and maritime air masses were dominant in the BL. The SEA air constitutes 15%, 45%, and 60% of the sampled air masses in the BL, LT, and MT, respectively. In the LT and MT, the dominant SEA air masses were transported from over peninsular SEA. Some of them had passed over northern India. In the MT, air from the tropical region (0°-10°N) was more frequently transported to the study region than in the LT, as seen in Figure 4b.

Trajectories of SEA and maritime air masses were combined with the cloud height data determined by the GMS-IR data to investigate the influence of convection on these air masses, as was done previously [*Miyazaki et al*., 2002]. Most of the trajectories of air masses sampled below 4 km encountered convective clouds within 4 days prior to sampling, as shown in Figure 5. In accordance with this analysis, some of the LT and MT trajectories show ascending motion due to convective transport, as shown in Figures 4b and 4c. These results indicate that SEA air masses sampled in the LT and MT were transported aloft from the BL over Southeast Asia by convection, and therefore had chances to be impacted by biomass burning.

BL air from SEA was rarely transported to the sampling region without significant changes in altitude. Part of the LT and MT air aloft from the BL of SEA moved

downward during eastward transport. Most of the SEA air masses sampled in the BL followed this pathway as seen in Figure 4a.

Most of the NEA air masses sampled in the BL were transported from Eurasia by strong northwesterly winds associated with the Siberian anticyclone and descended from the free troposphere down to the BL near the east coast of China around 25°-35°N (Figure 4a), suggesting the possible influence of northeastern China on these air masses, consistent with the chemical data shown in section 5.2.

5. Impact of Biomass Burning on Reactive Nitrogen and O_3

5.1. Vertical Profiles

Profiles of the median values of O_3, CO, H_2O, CH_3Cl, C_2Cl_4, and the major components of reactive nitrogen (NO_x, PAN, HNO_3, NO_3^-, and NO_y) for each air mass type are shown in Figure 6. The data below 1 km is not shown because of the scarcity of the data. Diurnally averaged OH concentrations were calculated with a box model [*Davis et al*., 1996; *Crawford et al*., 1997] using the observed NO, O_3, H_2O, NMHC, and $J(NO_2)$ values as input parameters and are also shown in Figure 6b.

The CH_3Cl mixing ratios were similar in the maritime and NEA air, indicating that these air masses were not significantly impacted by biomass burning. The CH_3Cl values in these air masses therefore represent background values. By contrast, the CH_3Cl values in the SEA air were much higher than these background values. The C_2Cl_4 values in the SEA air were similar to those in the maritime air at 2-11 km, indicating that SEA air was not significantly influenced by industrial activities.

The mixing ratios of the other trace gases, except for OH, were generally lowest in maritime air, reflecting a minimal influence of anthropogenic emissions on these air

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masses. OH concentration was highest in SEA air due to high humidity (Figure 6a), solar UV radiation, and NO (Figure 6b) which converts HO_2 to OH. The lifetime of NO_x is estimated to be 12 hours and 10 hours in the BL and LT, respectively, from this OH concentration.

The mixing ratios of O_3 and PAN values in NEA air masses were similar to or somewhat higher than those in SEA air, despite the possible effect of biomass burning on the SEA air masses. The latitudinal gradient of these species over the western Pacific, relatively free from biomass burning influences [e.g., *Kawakami et al.*, 1997; *Kondo et al.*, 1997b; 2002], indicates the relative abundances between these air masses. In order to estimate the impacts of biomass burning on SEA air, background values need to be determined as discussed in section 5.4.

5.2. SEA Air

5.2.1 CO as a Biomass Burning Tracer

CH_3Cl is a good parameter in representing the degree of primary emissions from biomass burning, as discussed in section 3. However, intervals between sampling can be as long as 5 minutes. On the other hand, CO, which is also emitted by biomass burning, was measured every 1 s. Figure 7 shows correlations of CH_3Cl and C_2Cl_4 with CO in SEA and NEA air masses in the LT. CO was correlated very well with CH_3Cl at all altitudes ($r^2 = 0.87$). Correlation of CO with C_2Cl_4 was poorer, especially in the LT ($r^2 = 0.22$). The slope of the CH_3Cl-CO correlation ($\Delta CH_3Cl /\Delta CO$) was 0.58 pptv/parts per billion by volume (ppbv), similar to the estimated emission ratio (ER) of 0.64 pptv/ppbv for biomass burning in savanna regions. The ER for tropical forest is

estimated to vary significantly in the range of 0.11-0.96 pptv/ppbv [*Andreae and Marlet*, 2001].

5.2.2 NO_x and PAN

Correlations of NO_x, PAN, HNO_3, NO_3^-, NO_x + PAN, HNO_3 + NO_3^-, and NO_y with CO in the BL, LT, and MT of the SEA and NEA air are shown in Figures 8a and 8b for the observed CO range of 80-500 ppbv, together with the regression lines, slopes, and correlation coefficients (r^2). The SEA data with H_2O mixing ratios lower than 1000 parts per million by volume (ppmv) are shown as blue dots for comparison. The median H_2O mixing ratios were higher than 1000 ppmv below 6 km (Figure 6a). These data represent dry air masses originating from the upper troposphere or those influenced by lower stratospheric air. 5-day back trajectories indicate that these air masses were transported from higher altitudes. The different characteristics of the dry air as compared with the typical SEA air is more clearly seen in the O_3-CO correlation for air masses sampled up to 8 km, as discussed in section 5.4. For this reason, the dry air data were excluded for the correlation analysis.

In the LT of SEA air, NO_x, PAN, NO_x + PAN, HNO_3, and NO_y were well correlated with CO with $r^2 = 0.52$-0.75, demonstrating that biomass burning was the predominant source of reactive nitrogen in these air masses. In the BL, $\Delta NO_x/\Delta CO$ in SEA air was slightly higher than in the LT and MT. It should be noted here that the BL air was transported downward from the LT, as discussed in section 4. PAN in LT air at temperatures of 275°-285°K should rapidly decompose releasing NO_2 when descending to the warmer BL at temperatures of 285°-295°K. The median lifetimes of PAN in the BL, LT, and MT calculated from the observed median temperatures are 10 hours, 1 day,

and 6-40 days, respectively. The median lifetime of NO_x against gas-phase oxidation by OH is estimated to be 12 hours and 10 hours in the BL and LT, respectively. The median NO_x production rate by PAN decomposition in the BL is calculated to be as high as 40 pptv hour^{-1} for the median PAN values. Therefore, the decomposition of PAN in the BL should significantly contribute to the higher $\Delta NO_x/\Delta CO$ value in the BL than in the LT.

In the MT, $\Delta NO_x/\Delta CO$ in SEA air was lower than that in the LT by a factor of 3, likely due to oxidation of NO_x and the lack of additional supply during upward transport from the LT to MT. PAN was well correlated with CO at all altitudes. In addition, $\Delta PAN/\Delta CO$ changed little during upward transport from LT to MT due to the chemical stability of PAN at low temperatures and its low solubility in water.

5.2.3 HNO$_3$, NO$_3^-$, and NO$_y$

HNO$_3$ is produced by gas-phase oxidation of NO_2 during daytime and hydrolysis of N_2O_5 on aerosols during nighttime. In the free troposphere, HNO_3 is removed by uptake by cloud droplets because of high water solubility, followed by precipitation. Uptake by dust particles, followed by sedimentation is another pathway of HNO_3 loss. HNO_3 also condenses on existing aerosols, which can be removed by precipitation after growing into cloud droplets. Nitrate measured on board the DC-8 includes particles larger than those on the P-3B, as discussed in section 2. Nitrate concentrations observed on the DC-8 were systematically higher than those observed on the P-3B in the BL of NEA, suggesting uptake of HNO_3 on coarse particles [*Jordan et al.*, 2003]. However, in SEA air, a majority of aerosol observed in the size range of 0.1-20μm by the optical counter [*Clarke et al.*, 2003] was in the fine mode (less than 1 μm).

Dominance of fine particles is typical for biomass burning plumes as observed, for example, in Brazil [*Reid and Hobbs*, 1998]. It has been found that nitrate was abundant in the fine-mode aerosol but not in coarse particles in SEA air (not shown). In addition, nitrate concentrations observed on the DC-8 and P-3B did not show any systematic difference, although the number of the DC-8 data was much smaller. These results indicate that coarse particles were not an important sink of HNO_3 in the SEA air. In the LT, the NO_3^- mixing ratio occasionally reached as high as 1000 pptv, which was close to the maximum gas-phase HNO_3 mixing ratio at a CO mixing ratios of 400 ppbv, indicating active conversion of HNO_3 into NO_3^-.

$\Delta HNO_3/\Delta CO$ ($\Delta(HNO_3 + NO_3^-)/\Delta CO$) decreased from 3.4 (3.3) pptv/ppbv in the LT to 0.71 (0.43) pptv/ppbv in the MT, although the scatter in the $(HNO_3 + NO_3^-)$-CO correlation was large in the MT. The regression line of the $(HNO_3 + NO_3^-)$-CO correlation passes through points close to the background values of CO = 84 ppbv and $(HNO_3 + NO_3^-) = 130$ pptv, which was determined independently, as discussed in section 5.4. This suggests that the slope determined above is reasonable despite the low r^2 value. The change in the slope corresponds to a loss of HNO_3 ($HNO_3 + NO_3^-$) of 79% (87%). The NO_y-CO correlation is much tighter than the $(HNO_3 + NO_3^-)$-CO correlation because NO_y is conserved to a greater degree than $HNO_3 + NO_3^-$. $\Delta NO_y/\Delta CO$ decreased from 7.3 pptv/ppbv in the LT to 3.0 pptv/ppbv in the MT, corresponding to a 59% loss of NO_y. This loss agrees well with the predicted NO_y decrease of 44% assuming an $HNO_3 + NO_3^-$ loss of 87% and an initial $(HNO_3 + NO_3^-)/NO_y$ ratio in the LT of 0.5 (Figure 6). Removal of $HNO_3 + NO_3^-$ in the free troposphere should occur by precipitation during upward transport. The altitude of water vapor saturation of the LT air was estimated assuming average temperature profiles measured

on board the P-3B and DC-8. Clouds are anticipated to form at about 4-5 km if the LT

air masses continue to move upward adiabatically, consistent with the observed large

loss of $HNO_3 + NO_3^-$ around this altitude. However, no quantitative relationship

between the decreased H_2O and NO_y (or $HNO_3 + NO_3^-$) amounts was found. Although

removal of H_2O should be associated with removal of HNO_3 in general, the rate of

HNO_3 removal will not necessarily be proportional to that of H_2O. Efficient removal of

HNO_3 has been shown to occur in tropical deep convection by calculation using a one-

dimensional model [*Mari et al.*, 2000]. *Mari et al.* predicted that about 80% of HNO_3 is

scavenged by warm and glaciated cloud, very similar to the present analysis.

The average $\Delta NO_y/\Delta CO$ of 7.3 pptv/ppbv in the LT is about 1/3 of the NO_x/CO ER

of 20.1 pptv/ppbv for biomass burning in SEA [*Streets et al.*, 2003], suggesting a

transport efficiency ε (NO_y) for the LT air to be 36%. Here ε (NO_y) is defined as the

average probability of transport of NO_x molecules from one region to another [*Koike et

al.*, 2003; *Miyazaki et al.*, 2003]. At CO mixing ratios lower than 300 ppbv,

$\Delta NO_y/\Delta CO$ is 5.4 pptv/ppbv, which is 25% smaller than the average. The ε (NO_y) for

the MT air decreased to 15%.

The ε (NO_y) from the BL to the free troposphere over the western Pacific during the

TRACE-P period was derived by *Koike et al.* [2003] and *Miyazaki et al.* [2003]. The ε

(NO_y) from the East Asian BL to the LT and MT at 30°-42°N was statistically estimated

by *Koike et al.* [2003] and is compared with the present value in Table 1, together with

the NO_x/CO ER. Major sources of NO_x and CO over the Asian continent at

midlatitudes are estimated to be combustion of fossil fuel and biomass. The LT value

by *Koike et al.* is lower than the present value by a factor of 3, although the MT value is

in good agreement. ε (NO_y) can depend on the oxidation rate of NO_x and frequency and

speed of upward transport. These different conditions and uncertainties controlling ε

(NO_y) might have caused the difference in the LT.

5.3. NEA Air

   The NEA air masses were most frequently sampled in the BL, and it is likely that

they were influenced by emissions of pollutants from the coastal area of China as

suggested in section 4. In the BL, $\Delta NO_x/\Delta CO$, $\Delta PAN/\Delta CO$, and $\Delta NO_y/\Delta CO$ of the

NEA air masses were much higher than those of the SEA air, demonstrating the distinct

difference in the chemical characteristics of these air masses from SEA. $\Delta NO_y/\Delta CO$ of

13.5 pptv/ppbv is 2-5 times larger than that in the BL and LT of SEA air masses.

However, the NO_x/CO ER for China for energy, industry, and agriculture is also as high

as 64.1 pptv/ppbv, which is 3 times larger than that of 20.1 pptv/ppbv for biomass

burning in SEA [*Streets et al.*, 2003]. As a result, transport efficiency of NO_y within the

BL is estimated to be 21%, assuming that most of the NO_y and CO were emitted over

the coastal region of China. Because the air masses remained in the BL after descent

over China, the loss of NO_y is most likely due to dry deposition of HNO_3 on the surface.

Uptake of HNO_3 by dust particles can also deplete NO_y, especially over Northern China

including the Yellow Sea region, as suggested by *Jordan et al.* [2003].

   Higher PAN values in the NEA than in the SEA is consistent with latitudinal

variation of PAN, which is strongly controlled by temperature [e.g., *Kondo et al.*,

1997b]. NO_x can be efficiently produced by thermal dissociation of PAN in the study

region.

5.4. Assessment of Biomass Burning Impacts on O_3 Precursors

Increases in the mixing ratios of O_3 precursors from biomass burning emissions in
SEA air masses can be assessed by defining their background levels. For this purpose,
the background level for CO in SEA air was determined using the correlation of C_2Cl_4
and CH_3Cl in SEA and NEA air masses, shown in Figure 9. In NEA air masses, C_2Cl_4
was enhanced independent of CH_3Cl due to the negligible impact of biomass burning.
The median level of CH_3Cl in NEA was close to the lowest CH_3Cl levels in SEA air
masses. Here threshold CH_3Cl levels for background air were chosen to be the 80
percentile of the CH_3Cl values for the NEA air (shown as a red line in Figure 9). They
were 610, 580, and 566 pptv in the BL, LT, and MT and these values were then
transformed to the corresponding CO values in SEA air. The resulting threshold CO
values were 198 ppbv, 131 ppbv, and 88 ppbv, respectively.

The background level X^B of a species X was defined as the median value of the
mixing ratios lower than these thresholds. Similarly, the impacted value X was defined
as the median value of the mixing ratios higher than the threshold. Profiles of X and X^B
for CO, major reactive nitrogen species, and O_3 are shown in Figure 10. The
uncertainty of X^B is largest for the BL air because of the scarcity of the data. The net
increase $\delta X = X - X^B$ is summarized in Table 2. ε (NO$_y$) can also be derived from
$\delta NO_y/\delta CO$ and the derived values are compared with those derived from $\Delta NO_y/\Delta CO$ in
Table 1. Both ε (NO$_y$) values are similar, indicating consistency of the present analysis.

CO is emitted directly from biomass burning and is largely conserved prior to
sampling because of its lifetime of about a month. Although NO$_y$ is also directly
emitted, it undergoes removal. It can be seen from Figure 10 that the impact of biomass
burning on CO and NO$_y$ was greatest in the LT with $\delta NO_y = 580$ pptv. δPAN and

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δHNO_3 made comparable contributions to δNO_y and the sum of these constituted 80% of δNO_y. The rest of δNO_y was due to δNO_x and δNO_3^-.

The observed PAN values in the BL and LT were due almost entirely to biomass burning because the background level for PAN was very low. In the MT, 75% of the observed PAN was due to biomass burning with $\delta PAN = 90$ pptv. By contrast, δNO_x and δHNO_3 were close to zero, demonstrating the important role of PAN in the long-range transport of reactive nitrogen emitted by biomass burning.

5.5. O_3 Production

The impact of biomass burning on O_3 was investigated in a similar way to that applied to reactive nitrogen. Correlations of O_3 with CO in the BL, LT, and MT of the SEA and NEA air masses are shown in Figure 11. The data of upper tropospheric origin with H_2O mixing ratios less than 1000 ppmv are shown as blue dots. The O_3 mixing ratios in SEA air masses were well correlated ($r^2 = 0.30$-0.59) with the CO mixing ratios throughout the whole altitude range, indicating the impact of biomass burning on O_3. $\Delta O_3/\Delta CO$ in the LT and MT was similar (about 0.16 ppbv/ppbv), indicating that O_3 was not produced during transport from the LT to MT, but was produced below the LT. This point was further investigated by calculating the photochemical production (P), loss (L), and net production (P - L) rates using the same box model as that used for OH calculation, as shown in Figure 12. For the region of this study, diurnally averaged P and L terms are expressed as

$$P = \left\{ k_{NO+HO_2}\left[HO_2\right] + k_{CH_3O_2+NO}\left[CH_3O_2\right] \right\}[NO] \qquad (1)$$

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$$L = \left\{ k_{H_2O+O(^1D)} J(O^1D) f[H_2O] + k_{OH+O_3}[OH] + k_{HO_2+O_3}[HO_2] \right\} [O_3] \qquad (2)$$

where [ ] denotes the concentration of the indicated species, k_{X+Y} is the reaction rate coefficient for the reaction $X + Y \rightarrow$ products, $J(O^1D)$ is the photolysis rate coefficient of O_3, and f is defined so that $J(O^1D)$ f $[O_3]$ is $[O(^1D)]$.

The P and L values increase linearly with NO and O_3, respectively (equations (1) and (2)). P increased with CO in the LT and MT, because NO_x and therefore NO increased with CO (Figure 8a). The L values also increased linearly with CO, because O_3 increased with CO. As a result, the P - L values were close to zero or slightly negative in the LT and MT, consistent with the similarity in the $\Delta O_3/\Delta CO$ in the LT and MT. From these results, it is very likely that most of the enhanced O_3 in the biomass burning plumes were produced before transport to the free troposphere. Because the air sampled in the BL was transported down from the LT, this point cannot be proven by the P - L values in the BL. In support of this analysis, surface O_3 mixing ratios were observed to increase from 10-20 ppbv in June-December period (wet season) to 40-55 ppbv in March-May period (dry season/transition period) at Inthanon (18.5°N, 98°E, 1450 m above sea level) and Srinakan (14°N, 99°E, 296 m asl) in Thailand due to biomass burning over SEA [*Pochanart et al.*, 2001; 2003]. The average daytime $\Delta O_3/\Delta CO$ value obtained at Srinakarin during the period between February and April for the years 1998, 1999, and 2000 was 0.10±0.03 for CO and O_3 ranges of 100-800 ppbv and 10-90 ppbv, respectively (P. Pochanart; private communication, 2003). This slope is considered to be close to the present value of 0.16 in the LT considering loss of O_3 by deposition at the surface.

The $\Delta O_3/\Delta CO$ for SEA air masses is compared with that obtained in other subtropical

burning regions and is summarized in Table 3. The data over northern Australia were

obtained in the boundary layer (< 3 km) during the Biomass Burning and Lightning

Experiment (BIBLE)-B in September [*Takegawa et al.*, 2003b]. The data in

Africa/South America were obtained at 1-6 km during TRACE-A [*Mauzerall et al.*,

1998] and at 0.5-6 km during the Southern African Regional Science Initiative 2000

(SAFARI 2000) [*Hobbs et al.*, 2003; *Yokelson et al.*, 2003]. It is remarkable that the

$\Delta O_3/\Delta CO$ values in fire plumes in different regions after 0.5-3 days following emissions

are similar to within a factor of 2, considering possible variability in the conditions for

photochemical O_3 production and loss by deposition. In all the measurements over

Australia and Africa/South America, buildup of O_3 occurred near the fires within a half

day, before O_3 precursors (such as NO_x and NMHCs) were consumed and diluted.

$\Delta O_3/\Delta CO$ remained nearly constant during transport in the BL over northern Australia

for a few days [*Takegawa et al.*, 2003b], supporting comparison of $\Delta O_3/\Delta CO$ observed

in air masses with different ages (0.05-4 days). In order to understand this similarity in

terms of photochemistry, we estimated the net number of O_3 molecules produced per

NO_x molecule oxidized (or emitted), known as the O_3 production efficiency (OPE). The

notion of OPE was first introduced by *Liu et al.* [1987] to estimate O_3 formation rates

over the U.S. continent. Here OPE (net number of O_3 molecules produced per NO_x

molecule emitted) has been derived by dividing $\Delta O_3/\Delta CO$ by NO_x/CO ER as was done

by *Chin et al.* [1994]. The NO_x/CO ER and OPE are given in Table 3. The NO_x/CO

ER and C_2H_4/CO ER for SEA were derived from the sum of emissions of NO_x, CO, and

C_2H_4 by burning of savanna/grasslands, forest, and crop residue in Thailand, Myanmar,

Laos, Cambodia, Vietnam, and Malaysia for 2000 [*Streets et al.*, 2003]. The ERs for

other regions are based on in situ measurements in fresh plumes. OPE is controlled by NMHC concentrations at high NO_x levels (hydrocarbon-limited) [e.g., *Liu et al.*, 1987; *Sillman et al.*, 1990]. C_2H_4 is one of the major NMHCs emitted from biomass burning [e.g., *Shirai et al.*, 2003 and references therein; *Yokelson et al.*, 2003] and is an important precursor for efficient O_3 production. The average OPE for savanna fire is 7.2±4.3 and varies to within a factor of about 2. A somewhat lower OPE for South Africa [*Yokelson et al.*, 2003] corresponds to a lower C_2H_4/NO_x ER.

OPE was also derived by using $\Delta O_3/\Delta(NO_y - NO_x)$ for urban plumes [e.g., *Chin et al.*, 1994; *Hirsch et al.*, 1996; *Rickard et al.*, 2002, and references therein] to estimate the net number of O_3 molecules produced per NO_x molecule oxidized. It is known that OPE estimated by using $\Delta O_3/\Delta CO$ is lower than that estimated by using $\Delta O_3/\Delta(NO_y - NO_x)$ because of deposition of HNO_3, which constitutes a major fraction of $NO_y - NO_x$ [e.g., *Chin et al.*, 1994; *Hirsch et al.*, 1996; *Ryerson et al.*, 2001; *Rickard et al.*, 2002, and references therein]. Therefore the OPE derived here should be considered a lower limit. The values of $\Delta O_3/\Delta CO$, ER, and OPE for urban plumes in the U.S. are given in Table 3 for comparison. NO_x/CO ER was estimated to have increased linearly from 140±60 pptv/ppbv in 1990 to 200±80 pptv/ppbv in 2000 [*Parrish et al.*, 2002; D. D. Parrish, unpublished results, 2003]. C_2H_4/NO_x ER was derived from the National Acid Precipitation Assessment Program (NAPAP) inventory for the U.S. in 1995 [*Saeger et al.*, 1989] and the U.S. Environment Protection Agency report for 2003 (http://www.epa.gov/ttn/chief/trends01/trends2001.pdf) (D. D. Parrish, unpublished results, 2003). The OPE for an urban plume is lower by a factor of 2-4 than that for a biomass burning plume despite the higher $\Delta O_3/\Delta CO$ ratio. This is due to a much higher NO_x/CO ER and a much lower C_2H_4/NO_x ER, which is typical for fossil fuel

combustion at high temperatures. High NO_x with an insufficient supply of NMHCs reduces OPE, as observed in power plant plumes [*Ryerson et al.*, 2001].

A net increase in O_3 was assessed as shown in Figure 10; in the BL, LT, and MT, δO_3 = 18, 19, and 22 ppbv, respectively. $O_3{}^B$ decreased from 40 ppbv in the LT to 25 ppbv in the MT. Air transported from tropical latitudes was sampled more frequently at higher altitudes in the MT, as discussed in section 4. The $O_3{}^B$ of 25 ppbv is similar to the median O_3 value for maritime air shown in Figure 6. As a result, $\delta O_3/O_3{}^B$ was 0.5 and 0.8 in the LT and MT, respectively. From these δO_3 values, we have estimated the O_3 flux from SEA to the western Pacific caused by biomass burning. Air impacted by biomass burning was transported from SEA to the Pacific along westerlies, mostly at the latitude range of 17°-30°N, as seen from the wind vectors shown in Figure 3. O_3 flux across the meridional plane at 0-8 km along 120°E at 17°-30°N was calculated as

$$F\left(\delta O_3\right) = \delta O_3 \times n_a \times U \times \eta \times f \times S \qquad\qquad (3)$$

where n_a is air number density, U is the average westerly component of the wind velocity given from the ECMWF data during TRACE-P, η is the probability of sampling the SEA air excluding low-H_2O data, f is the fraction of biomass burning-impacted air for the sampled SEA air masses, and S is the cross section of the meridional plane. These values at different altitudes are given in Table 4. η maximized in the LT and decreased with altitude, and f was almost independent of altitude. The O_3 flux in the BL was very small due to weak and unstable westerlies. The estimated F (δO_3) is 64 Gg O_3 day^{-1}.

On the other hand, the total O_3 production rate over peninsular SEA can be derived independently, assuming that $\Delta O_3/\Delta CO$ is uniform (0.16 ppbv/ppbv) for all biomass burning-impacted air. The total CO emitted from SEA was estimated to be 20270 Gg CO yr^{-1} for the year of 2000 [*Streets et al.*, 2003]. All of the SEA air masses used for the present analysis were sampled in March 2001. Considering that CO emissions in March constituted 46% of the total annual emission for 1997-2001 (Figure 1b), the emission rate in March is directly given as 303 Gg CO day^{-1}. This is transformed to a total O_3 production rate of 83 Gg O_3 day^{-1}. The F(δO_3) derived above constitutes 77% of the estimated total O_3 production rate, suggesting that a majority of O_3 produced in SEA was transported to the western Pacific.

In order to assess the overall accuracy of the derived O_3 flux, comparison was made with a value derived independently. O_3 fluxes in different types of air masses during TRACE-P were estimated using O_3 data obtained by lidar on board the DC-8 [*Browell et al.*, 2003]. Air masses characterized by high O_3 and low aerosol (HO3 category) in this study basically correspond to SEA air, and the O_3 flux of HO3 peaked at 26°N. The O_3 flux for HO3 air was integrated over the latitude range of 17°-30°N and the altitude range of 0-8 km resulting in 104 Gg O_3 day^{-1}. For comparison with this flux, δO_3 in equation (3) needs to be replaced with the median values of O_3 impacted by biomass burning (O_3).

$$F (O_3) = O_3 \times n_a \times U \times \eta \times f \times S. \qquad (4)$$

The F (O_3) was estimated to be 166 Gg O_3 day^{-1}, which is 60% higher than that estimated by *Browell et al.* [2003]. These values are in reasonable agreement,

considering some differences in the sampling regions for the P-3B and DC-8 and in the criteria defining biomass burning-impacted air masses.

6. Conclusions

Biomass burning activity was high over SEA (Thailand, Myanmar, Laos, Cambodia, Vietnam, and Malaysia) during the dry season of February-April 2001, when TRACE-P aircraft measurements were made. Convective activity over SEA, indicated by cloud images, frequently transported boundary layer air impacted by biomass burning to the free troposphere, followed by eastward transport to the sampling region over the western Pacific south of 30°N. As a result, air masses with enhanced CH_3Cl but low in C_2Cl_4 were frequently observed in the study region (17°N-30°N, 110°-150°E). We selected air masses transported from the intense burning region south of 28°N using five-day backward trajectories and defined them as SEA air in order to evaluate the impact of biomass burning on O_3 and its precursors (CO and reactive nitrogen). NEA air masses were defined as those transported from north of 28°N over the Asian continent to the study region at 17°N-30°N. The SEA air constitutes 15%, 45%, and 60% of the sampled air masses in the boundary layer (BL; 0-2 km), lower troposphere (LT; 2-4 km), and middle troposphere (MT; 4-8 km), respectively.

CH_3Cl and CO, which were well correlated with HCN and CH_3CN, were chosen as a primary and secondary tracers, respectively, to gauge the degree of impact of emissions of trace species from biomass burning. Biomass burning has been found to be a predominant source of reactive nitrogen (NO_x, PAN, HNO_3, and nitrate) and O_3 in this region from tight correlations of these species with CO ($r^2 = 054$-0.80) in the LT. Because of these tight correlations in the LT, we were able to quantify changes in the

abundance of reactive nitrogen during upward transport from the changes in the slopes of the correlations. $\Delta NO_x/\Delta CO$ was highest in the BL due to the decomposition of PAN during descent from the free troposphere to the BL. $\Delta NO_x/\Delta CO$ decreased by a factor of 5 from the LT to MT, due to oxidation and lack of additional supply of NO_x during upward transport. PAN was correlated well with CO at all altitudes with little change in $\Delta PAN/\Delta CO$ due to the low water solubility of PAN and its chemical stability in the free troposphere.

The average $\Delta NO_y/\Delta CO$ of 7.3 pptv/ppbv is about 1/3 of the NO_x/CO ER of 20 pptv/ppbv for biomass burning in SEA, indicating the transport efficiency from the BL to the LT to be about 36%. Half of the NO_y remaining in the LT was lost during transport from the LT to MT. The loss of NO_y was due to the 80-90% removal of $HNO_3 + NO_3^-$ by precipitation during upward transport.

Net increases in the mixing ratios of O_3 precursors were assessed by defining their background values using tracers. The net increases in CO and NO_y, which are directly emitted by biomass burning, were largest in the LT. Increases in PAN and HNO_3 constituted dominant parts of the NO_y increase of 570 pptv. In the MT, only PAN among the NO_y species showed substantial increase (80 pptv), demonstrating its important role in the long-range transport of reactive nitrogen emitted by biomass burning.

$\Delta O_3/\Delta CO$ was similar in the LT and MT, indicating that effective O_3 production due to biomass burning had occurred in the BL. Consistently, the net in situ O_3 production rate calculated by a box model was close to zero. $\Delta O_3/\Delta CO$ and O_3 production efficiency are very similar to those in fire plumes over northern Australia and Africa/South America. This relationship should be useful in understanding and

assessing the impact of biomass burning on O_3, including model studies. Net O_3 increases were 19-22 ppbv in LT and MT. The net O_3 flux across the 120°E meridional cross-section at 17°-30°N was estimated to be 64 Gg O_3 day^{-1} in March. On the other hand, the total O_3 production rate in SEA was estimated to be 83 Gg O_3 day^{-1}, suggesting that majority of O_3 produced in SEA was transported to the western Pacific.

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Figure Captions

Figure 1. (a) Distribution of hot spots from February 1 to April 30, 2001 observed by the Along Track Scanning Radiometer (ATSR)-2. (b) Monthly median hot spot numbers in the region of 10°-30°N and 70°-120°E between 1997 and 2001 (solid circles). The bars indicate the central 67% values. The data for 2001 are shown as open squares.

Figure 2. Horizontal distributions of CH_3Cl and C_2Cl_4 in the LT observed during the TRACE-P period. The study region is marked as rectangles.

Figure 3. The mean flow patterns at 500 hPa, 700 hPa, and 850 hPa in March 2001. Thin lines and arrows indicate stream lines and wind vectors, respectively. The study region is marked as rectangles.

Figure 4a. Five-day backward trajectories starting from the sampling point (closed circles) in the BL.

Figure 4b. Same as Figure 4a, but for the LT.

Figure 4c. Same as Figure 4a, but for the MT.

Figure 5. Probability of cloud encounter of air mass trajectories starting from the BL, LT, and MT as a function of time elapsed.

Figure 6a. Vertical profiles of the median mixing ratios of O_3, CO, H_2O, CH_3Cl, and C_2Cl_4 in SEA, NEA, and maritime air. The bars indicate the central 67% values.

Figure 6b. Same as Figure 6a, but for NO_x, HNO_3, PAN, NO_3^-, NO_y, NO_3^-, and OH.

Figure 6c. Same as Figure 6a, but for NO_x/NO_y, PAN/NO_y, and $(HNO_3 + NO_3^-)/NO_y$, ratios.

Figure 7. Correlation plots of CH_3Cl and C_2Cl_4 versus CO in the LT of SEA air.

Figure 8a. Correlation plots of NO_x, PAN, and NO_x + PAN versus CO in the BL, LT, and MT of SEA (red solid circles) and NEA (open circles) air. Data with H_2O mixing ratio higher than 1000 ppmv are shown as blue crosses.

Figure 8b. Same as Figure 8a, but for HNO_3, NO_3^-, HNO_3 + NO_3^-, and NO_y.

Figure 9. Correlation plot of C_2Cl_4 versus CH_3Cl in SEA and NEA air. The threshold CH_3Cl level for background air were chosen to be the 80 percentile of the CH_3Cl values for the NEA air (red line). The 90 percentile of the C_2Cl_4 values for the SEA air is shown for reference (black line).

Figure 10. Vertical profiles of the median mixing ratios of O_3, CO, NO_x, HNO_3, PAN, NO_3^-, HNO_3 + NO_3^-, and NO_y for biomass burning-impacted (closed circles) and background air (open squares). The bars indicate the central 67% values.

Figure 11. Correlation plots of O_3 versus CO in the BL, LT, and MT of SEA (red solid circles) and NEA (open circles) air. SEA data with H_2O mixing ratio higher than 1000 ppmv are shown as blue crosses.

Figure 12. O_3 production rate (P), loss rate (L), and net O_3 production rate (P - L) as a function of CO in the BL, LT, and MT.

Table 1. Transport Efficiency of NO_y (ε (NO_y))

Study region	ER (NO_x/CO)	ε (NO_y) at 2-4 km	ε (NO_y) at 4-7 km
Present study (A): 17°-30°N	20	0.36	0.15
Present study (B): 17°-30°N	20	0.30	0.20
Koike et al. [2003]: 30°-42°N	53	0.10±0.02	0.15±0.03

Emission Ratios (ER) are given in pptv/ppbv.

Present study (A): derived from $\Delta NO_y/\Delta CO$, (B): derived from $\delta NO_y/\delta CO$ (see text for details)

Table 2. Median Values of O_3, CO, and Reactive Nitrogen in SEA Air above Thresholds.

Species	0-2 km	2-4 km	4-6 km	6-8 km
O_3 (ppbv)	57 (17)	58 (19)	49 (19)	50 (24)
CO (ppbv)	268 (78)	205 (98)	118 (36)	111 (26)
NO_x (pptv)	133 (85)	74 (32)	33 (14)	43 (26)
HNO_3 (pptv)	510 (95)	417 (271)	160 (41)	95 (20)
NO_3^- (pptv)	59 (26)	37 (37)	0 (0)	0 (0)
$HNO_3 + NO_3^-$ (pptv)	623 (78)	440 (220)	197 (37)	154 (56)
PAN (pptv)	234 (204)	213 (196)	135 (99)	106 (77)
NO_y (pptv)	873 (190)	963 (581)	415 (137)	416 (125)

CO thresholds: 224 ppbv (BL), 131 ppbv (LT), and 88 ppbv (MT).

The numbers in parentheses are the median values of the increase in the mixing ratio of species X (δX in the text).

Table 3. $\Delta O_3/\Delta CO$, Emission Ratios (ER), and Ozone Production Efficiency (OPE) for Biomass Burning

Location	Ref	$\Delta O_3/\Delta CO$	Altitude (km)	Age (days)	ER (NO_x/CO)	ER (C_2H_4/NO_x)	OPE
This study	1, 2	0.16(±20%)	2-8	2-3	21(±190%)	0.96(±140%)	7.6(±190%)
Australia	3, 4	0.12(±30%)	1-3	0.5-3	18(±10%)	0.38(±10%)	6.7(±30%)
South Africa	5, 6	0.09(±15%)	0.5-2	0.05	44(±20%)	0.22(±20%)	2.0(±25%)
South Africa	5, 6	0.22(±nil)	1-6	2-4	53(±30%)	0.26(±30%)	4.2(±30%)
Africa/S America	7	0.15(±250%)	0-4	0.5	13(±20%)	0.51(±40%)	11.5(±250%)
US and Europe	8, 9, 10, 11	0.30(±15%)	0	0.3	170(±40%)	7×10^{-5} (±30%)	1.8(±50%)

References: 1 : *Andrea and Marlet* [2001], 2: *Streets et al.* [2003], 3: *Takegawa et al.* [2003b] , 4: *Shirai et al.*, [2003], 5: *Yokelson et al.*, [2003], 6: *Hobbs et al.* [2003], 7: *Mauzerall et al.* [1998], 8: *Chin et al.* [1994], 9: *Hirsch et al.* [1996], 10: *Rickard et al.* [2002]. 11: Parrish et al. [2002]. ER (NO_x/CO) is given in pptv/ppbv and ER (C_2H_4/NO_x) is given in pptv/pptv. Uncertainties in the estimates due to measurement errors and natural variability ($1-\sigma$) are given wherever available.

Table 4. Parameters used for calculating the net O_3 flux

	0-2 km	2-4 km	4-6 km	6-8 km
U (m/s)	0.9	8.7	20.0	27.4
η	0.24	0.46	0.39	0.15
f	0.53	0.61	0.76	0.77

U: average westerly component of the wind velocity

η: probability of sampling the SEA air masses excluding low-H_2O data

f: fraction of biomass burning impacted air